

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

THIS PAGE BLANK (USPTO)

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶: C08F 10/00, 4/652	A1	(11) International Publication Number: WO 96/13531 (43) International Publication Date: 9 May 1996 (09.05.96)
(21) International Application Number: PCT/US95/13148 (22) International Filing Date: 18 October 1995 (18.10.95) (30) Priority Data: 08/331,439 31 October 1994 (31.10.94) US 08/479,963 7 June 1995 (07.06.95) US 08/543,991 17 October 1995 (17.10.95) US (71) Applicant: W.R. GRACE & CO.-CONN. [US/US]; 1114 Avenue of the Americas, New York, NY 10036 (US). (72) Inventor: WARD, David, G.; 8408 Woodland Manor Drive, Laurel, MD 20724 (US). (74) Agent: CAPRIA, Mary, Ann; W.R. Grace & Co.-Conn., 7500 Grace Drive, Columbia, MD 21044 (US).		(81) Designated States: AL, AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: PREPARATION OF MODIFIED POLYOLEFIN CATALYSTS AND IN SITU PREPARATION OF SUPPORTED METAL-LOCENE AND ZIEGLER-NATTA/METALLOCENE POLYOLEFIN CATALYSTS		
(57) Abstract Novel transition and rare earth metal catalysts that do not require the use of alumoxanes, methods for modifying transition or rare earth metal containing compounds that are capable of polymerizing olefinic monomer materials, methods for forming <i>in situ</i> supported metallocenes, supported Ziegler-Natta/metallocene catalysts are provided. Further included is a method for using the novel catalysts to prepare novel polymers.		

- 1 -

**PREPARATION OF MODIFIED POLYOLEFIN CATALYSTS AND
IN SITU PREPARATION OF SUPPORTED METALLOCENE
AND ZIEGLER-NATTA/METALLOCENE
POLYOLEFIN CATALYSTS**

5

This application is a continuation-in-part of U.S. Patent Application Serial No. 08/479,963 filed on June 7, 1995, which is a continuation-in-part of 08/331,439, filed on October 31, 1994.

10

Background

15

It has been known to use metallocene compounds of transition metals as catalysts for polymerization and copolymerization of olefins. Metallocenes are not polymerization catalysts by themselves, but must be activated with a cocatalyst. The most common cocatalysts are methyl alumoxanes (MAOs), which are oligomeric compounds containing Al-O-Al linkages prepared by the hydrolysis of trimethyl aluminum (TMAL). MAO's are extremely expensive because the TMAL is difficult to prepare and costs an order of magnitude more than the common triethyl aluminum (TEAL) used as a cocatalyst with Ziegler catalysts. MAO's are also more difficult to handle than TEAL due to their inherent instability and the high viscosity of their solutions.

20

25

The use of metallocene catalyst systems provides the ability to produce uniform polymers and copolymers of narrow molecular weight distribution (MWD) and narrow compositional distribution. The use of Ziegler-Natta

- 3 -

polyethylene or polystyrene. The metallocenes and alumoxanes are deposited on the dehydrated support material.

U.S. Patent No. 4,701,432 teaches a support treated with at least one metallocene and at least one non-metallocene transition metal compound. To form a catalyst system, a cocatalyst comprising an alumoxane and an organometallic compound of Group IA, IIA, IIIB, and IIIA is added to the supported metallocene/non-metallocene. The support is a porous solid such as talc or inorganic oxides or resinous material, preferably an inorganic oxide, such as silica, alumina, silica-alumina, magnesia, titania or zirconia, in finely divided form. By depositing the soluble metallocene on the support material, it is converted to a heterogeneous supported catalyst. The transition metal compound, such as $TiCl_4$, is contacted with the support material prior to, after, simultaneously with or separately from contacting the metallocene with the support.

A concern in the field of polyolefin manufacture is the ability to control the MWD of the resulting polymer.

Broad MWD have been linked to improved processability and improved performance in the resulting polymer. Single metallocene catalyst systems typically produce a narrow range of molecular weight. Some techniques such as multiple reactors and physical blending of polymers

catalysts that produce polymers with minimal side reactions and with optimal dispersion of catalytic centers on the support. Moreover, there is a need for a catalyst for olefin polymerization that can be produced
5 inexpensively while achieving a broad range of molecular weight, bimodal or multi-modal molecular weight distribution in the final polymers.

It is therefore desirable to develop a method that can produce a supported metallocene catalyst or a
10 combination supported Ziegler-Natta/metallocene catalyst in-situ ("one pot") that does not require the use of expensive MAOs while permitting sufficient process control to optimally and preferentially produce only supported metallocene or the mixed Ziegler-Natta/
15 metallocene catalyst systems.

It is also desirable to produce a catalyst that is capable of producing polymers with improved processing characteristics such as faster throughput out of
20 extrusion dies without increasing processing temperature or pressure and polymers with less chlorine residues that corrode polymer processing machinery and lower resin quality. Chlorine in the polymer causes discoloration and deterioration of polymer physical properties.

Accordingly, it is an object of the present
25 invention to provide novel methods for making supported metallocene in-situ and supported Ziegler-Natta/

- 7 -

Summary of the Present Invention

The present invention meets the above objectives by providing improved methods of modifying previously prepared and commercially available polyolefin chromium and Ziegler-Natta catalysts and mixtures thereof as well as manufacturing in-situ supported metallocene and supported Ziegler-Natta/metallocene mixed catalyst precursors.

The invention further provides unique catalyst compositions suitable for forming polymers having broad molecular weight distribution and good flow properties (i.e., the ability to be processed through dies and other machinery without raising the processing temperature or pressure). The polymers produced in accordance with the present invention also have reduced presence of polymer degrading and equipment corroding materials, such as chlorine, in the final polymer product.

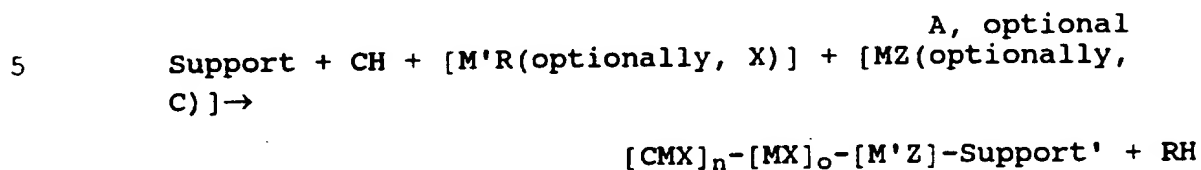
In one aspect, the invention encompasses the method to produce a novel catalyst precursor by modifying a previously prepared or commercially available polyolefin catalyst by treatment with the insitu technology defined herein.

In another aspect, the present invention provides a method to prepare in-situ a supported metallocene catalyst and a mixture of ZN/metallocene catalyst

- 9 -

organics and mixtures thereof, and optionally, containing an additional organic component that contains a five-member carbon ring, a heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as two
5 cyclic moieties capable of coordinating to the transition or rare earth metals;

(B) recovering the resulting supported catalyst precursor.

Illustration II (InSitu/InSitu)

The terms used in Illustrations I and II are defined below.

Support

The Support is optional and can be any sufficiently porous inorganic, inorganic oxide or organic material. Suitable inorganic materials include magnesium compounds or their complex salts such as MgCl_2 , $\text{MgCl}(\text{OEt})$ and $\text{Mg}(\text{OEt})_2$, organic magnesium compounds such as those represent by $\text{MgR}'_x\text{X}'_y$ wherein, R' is an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms or aryl group having 6 to 20 carbon atoms; x is a halogen atom or an alkyl group having 1 to 20 carbon atoms; x is a number from 0 to 2; and y is a number from 0 to 2. Inorganic oxide supports, including talcs, clays, and metal oxides from Groups 2-14, actinide, lanthanide series metals from the Periodic Table; suitable metal oxides are typically SiO_2 , Al_2O_3 , MgO , ZrO_2 , Fe_2O_3 , B_2O_3 , CaO , ZnO , BaO , ThO_2 and mixtures thereof; for example, silica-alumina, silica-titania, silica-titania-alumina, zeolite, ferrite, glass fibers,

Pore volume and surface area, for example, can be measured from volume of nitrogen gas adsorbed in accordance with BET method. (Refer to J. Am. Chem. Soc., Vol. 60, p. 309 (1983)).

5

C

10

C represents a ligand defined as one five-member carbon ring, heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as multi-cyclic moieties capable of coordinating to the transition or rare earth metals, M.

15

The ansa bridge can be selected from the group comprising carbon, silicon, phosphorus, sulfur, oxygen, nitrogen, germanium, species such as R''_2C , R''_2Si , R''_2Ge , $R''_2CR''_2C$, $R''_2SiR''_2Si$, $R''_2GeR''_2Ge$, $R''_2CR''_2Si$, $R''_2C R''_2Ge$, $R''_2CR''_2CR''_2C$, $R''_2SiR''_2Si$, diradicals where R is independently selected from the group containing hydride, halogen radicals, and C1-20 hydrocarbyl radicals including ethyl, propyl; preferred ansa bridges include Me_2Si (dimethylsilyl), $-Ph_2Si$ (diphenylsilyl), Me_2C (isopropylidene), Ph_2P (diphenylphosphoryl), $Me_2SiSiMe_2$ (tetramethyldisilane) and the like. Preferably, the ansa bridge has a length of two atoms or less as in methylene, ethylene, diphenylsilyl, dimethylsilyl, and methylphenylsilyl.

20

- 15 -

C20 alkyls such as ethyl, butyl, octyl, ethylhexyl);
aryls (preferably C6-C20 aryls such as phenyl, p-tolyl,
benzyl, 4-t-butylphenyl, 2,6-dimethylphenyl, 3,5-
methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl);
5 alkenyls (preferably C1-C20 alkenyls, such as ethenyl,
propenyl, butenyl, pentenyl); amides (preferably NR^aR^b ,
wherein the R^a and R^b can be the same or different and
independently selected from halosubstituted and non-
substituted alkyls, alkenyls, aryls, or silanes;
10 preferably C1-C20 alkyls and alkenyls and C6-C20 aryls,
including substituted aryls, such as ethyl, butyl, octyl,
ethylhexyl), phenyl, p-tolyl, benzyl, 4-t-butylphenyl,
2,6-dimethylphenyl, 3,5-methylphenyl, 2,4-dimethylphenyl,
2,3-dimethylphenyl); preferred amides are dimethylamide,
15 diethylamide, hexamethyldisilazide and mixtures of two or
more of the foregoing. More preferred R groups in the
 NR^aR^b are C1-C5 alkyls, C2-C5 alkenyls, phenyl and Naphthyl
and mixtures thereof.

X and Z may be the same or different and are
20 preferably chloride, bromide, ethoxy, and mixtures
thereof; wherein n is never 0. The n and o refer to
quantity (wt.% or molar ratio) and not the number of any
particular ligand. When o is zero, a supported
metallocene catalytic precursor system is achieved. When
25 n is any number greater than zero, a supported mixed

- 17 -

Preferred amides are dimethylamide, diethylamide, hexamethyldisilazide and mixtures of two or more of the foregoing.

5 PREFERRED CM'X AND CM', respectively

CM'X is preferably selected from the group comprising dicyclopentadienylethylaluminum, bis(pentamethylcyclopentadienyl)aluminumchloride, cyclopentadienylmagnesium chloride, dicyclopentadienyl
10 aluminumchloride, cyclopentadienylaluminumdichloride, dicyclopentadienylmagnesium, bisindenylethylaluminum, indenylmagnesiumchloride, bisindenylaluminum chloride, indenylaluminumdichloride, diindenylmagnesium, difluorenylethylaluminum, difluorenylaluminum,
15 fluorenylmagnesiumchloride, difluorenylaluminumchloride, fluorenylaluminumdichloride, difluorenylmagnesium and mixtures thereof.

A

20 A, may be optionally used to further modify the catalyst and/or support, and can be selected from the group comprising acid halides, (e.g., HCl, HBr and HI); metal halides (preferably, Al, Si, Sn, Ti, Mg, Cr wherein the halide are Cl, Br, I and mixtures thereof; organic
25 halides (R'X), carboxcyclic acids (R'(COOH)_n), esters (R'(COOR'')_n), ethers (R'(OR'')_n) when n is equal to or

- 19 -

magnesium chloride, and isopropyl magnesium bromide and mixtures thereof.

Additional suitable "A" compounds for use in this invention are halogen gas and alumoxanes.

5 Preferred A's include CH_3Cl , tetrahydrofuran, dibutylphthalate, t-butylchloride, dialkyl phthalates, ethanol, phenol, ethylaluminumdichloride, silicon tetrachloride, methyllithium, methylmagnesium chloride, dibutylphthalate, dibutylphthalate and tin tetrachloride;
10 halogen gases such as Cl_2 , F_2 , and Br_2 and mixtures of two or more of the foregoing.

SUPPORT'

The Support' can be the same as the Support (before any reaction takes place) or can be a modified Support as
15 a result of the occurring reaction. For example, when trimethylsilylcyclopentadiene ("TMSCp") or other silanizing agents are used, the silanizing agent reacts with the support to consume any residual hydroxyl that may be present.

20 Conditions of the reaction can vary causing the reaction product to be completely metallocene or a mixed ZN/metallocene catalyst system. The reaction can be carried over a broad range of temperatures, typically from approximately -78°C to 200°C , preferably at 0°C to
25 room temperature.

- 21 -

This reaction is illustrated by Illustration III as follows.

ILLUSTRATION III

[Preformed metallocenic, Ziegler-Natta
and/or Cr Catalysts,
which may be supported,
thereby containing
MZ(optionally, C)] + [CM'(optionally, X)]_n → Modified
Preformed
Catalyst

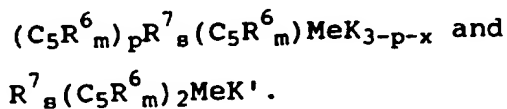
Illustrations I, II, and III above are carried out in the presence of a solvent in either a solution or a slurry. The solvents that are desirably utilized are solvents that do not adversely affect the preparation of the catalyst or, if any residue remains, does not adversely affect polymerization or the properties of the resulting polymer. Preferably, the solvent is a non-polar organic solvent; and most preferably includes aliphatic hydrocarbons (typically C3 to C12, such as butane, isobutane, pentane, isopentane, hexane, octane, decane, dodecane, hexadecane, octadecane, and the like); alicyclic hydrocarbons (typically C5-C20, such as cyclopentane, methylcyclopentane, cyclohexane, decalin cyclooctane, norbornane, ethylcyclohexane and the like); aromatic hydrocarbons, including substituted aromatics such as benzene, chlorobenzene, xylene, toluene and the like; and petroleum fractions such as gasoline, kerosene, light oils, and the like. It may also be desirable to

(isopropylidene), Ph_2P (diphenylphosphoryl) $\text{Me}_2\text{SiSiMe}_2$ (tetramethyldisilane) and the like. Preferably, the ansa bridge has a length of two atoms or less as in methylene, ethylene, diphenysilyl, dimethylsilyl, propylidene and methylphenylsilyl.

The transition metal component of the metallocene is selected from Groups 3 through 10, lanthanides and actinides series of the Periodic Table and mixtures thereof; and most preferably, titanium, zirconium, hafnium, chromium, vanadium, samarium and neodymium and mixtures thereof. Of these Ti, Zr, and Hf and mixtures thereof are most preferable.

In one preferred embodiment, the CMX metallocene catalyst precursor is represented by the general formula $(\text{Cp})_m \text{MR}^4_n \text{R}^5_p$, wherein Cp is a substituted or unsubstituted cyclopentadienyl ring, M is a Group 3-6, lanthanide, actinide series metal from the Periodic Table and mixtures thereof; R^4 and R^5 are independently selected halogen, hydrocarbyl group, or hydrocarboxyl groups having 1-20 carbon atoms; $m=1-3$, $p=0-3$ and the sum of $m+n+p$ equals the oxidation state of M.

In another embodiment the CMX is represented by the formulae:



dimethyl, bis(cyclopentadienyl)titanium diphenyl,
bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)zirconium diphenyl, bis(cyclopentadienyl)hafnium dimethyl and diphenyl, bis(cyclopentadienyl)titanium di-neopentyl,
5 bis(cyclopentadienyl)zirconium di neopentyl, bis(cyclopentadienyl)titanium dibenzyl, bis(cyclopentadienyl)zirconium dibenzyl, bis(cyclopentadienyl)vanadium dimethyl; the mono alkyl metallocenes such as bis(cyclopentadienyl)titanium methyl chloride, bis(cyclopentadienyl)titanium ethyl chloride, bis(cyclopentadienyl)titanium phenyl
10 chloride, bis(cyclopentadienyl)zirconium methyl chloride, bis(cyclopentadienyl)zirconium ethyl chloride, bis(cyclopentadienyl)zirconium phenyl chloride, bis(cyclopentadienyl)titanium methyl bromide; the trialkyl metallocenes such as
15 cyclopentadienyl titanium trimethyl, cyclopentadienyl zirconium triphenyl, and cyclopentadienyl zirconium trineopentyl, cyclopentadienyl zirconium trimethyl, cyclopentadienyl hafnium triphenyl, cyclopentadienyl hafnium trineopentyl, and cyclopentadienyl hafnium
20 trimethyl; monocyclopentadienyls titanocenes such as, pentamethylcyclopentadienyl titanium trichloride, pentaethylcyclopentadienyl titanium trichloride; bis(pentamethylcyclopentadienyl) titanium diphenyl, the carbene represented by the formula bis(cyclopentadienyl)titanium=CH₂ and derivatives of this reagent; substituted
25 bis(cyclopentadienyl)titanium (IV) compounds such as:

ntadienyl) (fluorenyl)hafnium dichloride, diisobutylmethyle
ne(cyclopentadienyl) (fluorenyl)hafnium dichloride,
ditertbutylmethylenecyclopentadienyl) (fluorenyl)hafnium
dichloride, cyclohexylidene(cyclopentadienyl)(fluorenyl)haf
5 nium dichloride, diisopropylmethylenecyclopentadienyl) (fluorenyl)hafnium
dichloride, isopropyl(cyclopentadienyl)(fluorenyl)titanium
dichloride, diphenylmethylenecyclopentadienyl)
(fluorenyl)titanium dichloride, diisopropylmethylenecyclop
10 entadienyl) (fluorenyl)titanium dichloride,
diisobutylmethylenecyclopentadienyl) (fluorenyl)titanium
dichloride, ditertbutylmethylenecyclopentadienyl)
(fluorenyl)titanium dichloride, cyclohexylidene(cyclopentad
ienyl) (fluorenyl)titanium dichloride,
15 diisopropylmethylenecyclopentadienyl) (fluorenyl)titanium dichloride,
racemic-ethylene bis (1-indenyl) zirconium (IV) dichloride,
racemic-ethylene bis (4,5,6,7-tetrahydro-1-indenyl)
zirconium (IV) dichloride, racemic-dimethylsilyl
bis (1-indenyl) zirconium (IV) dichloride, racemic-
20 dimethylsilyl bis (4,5,6,7-tetrahydro-1-indenyl) zirconium
(IV) dichloride, racemic-1,1,2,2-tetramethylsilanylene bis
(1-indenyl) zirconium (IV) dichloride, racemic-1,1,2,2-
tetramethylsilanylene bis (4,5,6,7-tetrahydro-1-indenyl)
zirconium (IV), dichloride, ethylidene (1-indenyl
25 tetramethylcyclopentadienyl) zirconium (IV) dichloride,
racemic-dimethylsilyl bis (2-methyl-4-tert-butyl-1-

- 29 -

dichloroethylenebisindenylzirconium, and dichloroethylene bis(tetrahydroindenyl)zirconium.

The CMX in this invention can also include non-cyclopentadienyl catalyst components (such as
5 pentadienyls) as well as ligands such as borollides or carbollides in combination with a transition metal.

POLYMERIZATION

The catalytic precursors prepared according to the
10 method of the present invention may be activated by any number of catalytic activators and used to polymerize olefinic materials.

The catalytic activators includes those represented by the formula $R^4_nAlX_{3-n}$ where R^4 is a hydrocarbon radical
15 having from 1 to about 20 carbon atoms, X is monovalent radical selected from the halogens and hydrogen, and n is an integer of 0-3. Examples of specific compounds include trimethylaluminum, triisobutylaluminum, tridodecylaluminum, tricyclohexyl aluminum,
20 triphenylaluminum, tribenzylaluminum, diethylaluminum chloride, ethylaluminum dichloride, isopropylaluminum dibromide, diisobutylaluminum hydride, and the like, and mixtures thereof.

While unnecessary to practice the present invention,
25 the catalytic activator may also include alumoxanes, such

ferroceniums and mixtures thereof; preferably carboniums and ferroceniums and mixtures thereof; and most preferably triphenyl carbenium. The $[C^+]$ may also include mixtures of the Bronsted acids and the abstracting moiety species.

[N] is selected from the group consisting of boron, phosphorus, antimony or aluminum and mixtures thereof, having the n valence state. Preferably, the [N] is boron, aluminum and mixtures thereof.

[Q₁-Q_{n+1}] are independent, wherein Q₁-Q_{n+1} are RX is defined wherein X is a halogen group element and is typically fluorine, chlorine, and bromine and mixtures thereof; preferred halogens are fluorine, chlorine, iodine and mixtures thereof; and most preferred is fluorine; and R is mono or multi-cyclic aryls, alkyls, and alkenyl groups and mixtures thereof; preferred are C1-20 alkenyl groups (such as ethene, propylene, butene, and pentene); C1-20 alkyl groups (such as a methyl, ethyl, n-propyl, iso-propyl, n-butyl, n-octyl, and 2-ethylhexyl groups), C6-20 aryl group (including substituted aryls) (such as phenyl, p-tolyl, benzyl, 4-t-butylphenyl, 2,6 dimethylphenyl, 3,5- methylphenyl, 2,4-dimethylphenyl, 2,3-dimethylphenyl groups) and mixtures thereof. More preferred R groups are C1-5 alkyls, C2-5 alkenyls phenyl and naphthyl and mixtures thereof.

- 33 -

and mixtures thereof. Preferred $N^n(Q_n)$ from the neutral species of the preferred list above of $[N^n(Q_1-Q_{n+1})]$.

Most preferred catalytic activators are organo aluminum co-catalysts such as TEAL, tri-methylaluminum, tri-isobutylaluminum, tri-n-octylaluminum, ethylaluminum dichloride, diethylaluminumchloride and the like; ionic cocatalysts from the boron family such as tris(pentafluorophenyl)borane, dimethylanilinium tetra(pentafluorophenyl)borate, triphenylcarbenium tetra(pentafluorophenyl)borate, and the like; and cocatalysts from the aluminate family such as dimethylanilinium tetra(pentafluorophenyl)aluminate, triphenylcarbenium tetra(pentafluorophenyl)aluminate and the like in conjunction with an alkylating agent such as an alkylaluminum or other organometallic and mixtures of all of the above activators.

The present invention is capable of polymerizing olefinic materials in a slurry phase polymerization reactor, such as a 2L Zipperclave under conditions as described in the examples below, achieving a catalytic activity of at least 10 grams of polyethylene per 1g catalyst used, without the use of an alkylalumoxane catalytic activator.

In general, however, the catalytic systems using the present invention are useful to polymerize olefinic materials, particularly ethylene. Polymerizations of

similar conditions to known olefin polymerization catalyst.

Typically, for the slurry process, the temperature is from approximately 0 degrees C to just below the temperature at which the polymer becomes soluble in the polymerization medium. For the gas phase process, the the temperature is from approximately 0 degrees C to just below the melting point of the polymer. For the solution process, the temperature is typically the temperature from which the polymer is soluble in the reaction medium up to approximately 275 degrees C.

The pressure used can be selected from a relatively wide range of suitable pressures, e.g., from subatmospheric to about 350 Mpa. Suitably, the pressure is from atmospheric to about 6.9 Mpa, or 0.05-10 Mpa, especially 0.14-5.5 Mpa. In the slurry or particle form process, the process is suitably performed with a liquid inert diluent such as a saturated aliphatic hydrocarbon. Suitably the hydrocarbon is a C4 to C10 hydrocarbon, e.g., isobutane, heptane or an aromatic hydrocarbon liquid such as benzene, toluene or xylene. The polymer is recovered directly from the gas phase process or by filtration or evaporation from the slurry process or evaporation from the solution process.

The catalyst of the present invention are particularly suited for the gas phase or slurry process.

Example 1-7 ("In-Situ Method")

A 20g aliquot of the desired support is weighed into a flask in an argon purged glove box. The sealed flask
5 is removed from the glove box and the support is slurried in approximately 200ml of hexane under an argon atmosphere using typical Schlenk techniques. The slurry is shaken at 0°C and a slurry of di(cyclopenta-
dienyl)magnesium ("Cp₂Mg") is added. The amounts of the
10 reagents are shown in Table A. Neat TiCl₄, is added and the mixture shaken an additional 15 minutes at 0°C. The resulting slurry is shaken overnight at room temperature.
A 10 second burst of HCl gas is admitted to the slurry and it is shaken an additional 15 minutes. The
15 supernatant is decanted and the solids washed with three, 75 ml aliquots of hexanes. The remaining solvents are removed *in vacuo*. The catalysts were used to polymerize olefins and the results are shown in Table C.

Example 1-7a--Comparison of In-Situ Preparation with
In-Situ treated with a Ziegler-Natta

5 The catalysts of samples 1, 2, 3, 5, 6, and 7 were
treated with 0.3 ml of TiCl_4/g catalyst and washed thrice
with excess hexanes. The catalysts were used to
polymerize olefins and the results are shown in Table C,
10 as samples 1a, 2a, 3a, 5a, 6a, and 7a.

Examples 8-11("In-Situ-In-Situ Method")

15 A 20g aliquot of the desired support is weighed into
a flask in an argon purged glove box. The sealed flask
is removed from the glove box and the support is slurried
in approximately 200ml of hexanes under an argon
atmosphere using typical Schlenk techniques. The slurry
is shaken at 0°C and of Cyclopentadiene is added. The
20 amounts of the reagents are shown in Table B. At 0°C ,
dialkylmagnesium (R_2Mg) is added. The slurry is shaken
for 1 hour at 0°C and an additional 2 hours at room
temperature. Neat TiCl_4 , is added and the mixture shaken
an additional 15 minutes at 0°C . The resulting slurry is
25 shaken overnight at room temperature. A 10 second burst
of HCl gas is admitted to the slurry and it is shaken an
additional 15 minutes. The supernatant is decanted and
the solids washed with three 75 ml aliquots of hexanes.
The remaining solvents are removed *in vacuo*.

TABLE C
Polymerization Results

Sample	Yield* (g)	Sample**	Yield* (g)
1	10	1a	6.2
2	0.1	2a	0.2
3	6.0	3a	4.4
4	6.0		
5	0.3	5a	1.7
6	0.15	6a	6.5
7	4.3	7a	10.6
8	0.9	8a	5.8
9	0.55	9a	2.7
10	8.5	10a	17.7
11	15.0	11a	16.6

* Yield = Grams of Polyethylene

** Sample Post Treated with TiCl_4

Examples 12 and 12a -- Comparison Cp_2Mg MODIFIED
PREFORMED CATALYST To UNMODIFIED CATALYST

A commercial silica supported Ziegler/Natta catalyst,
 $[(\text{TiCl}_4)\text{MgCl}_2\text{-SiO}_2]$ was prepared separately and modified
 with Cp_2Mg by mixing the ZN catalyst with the Cp_2Mg in
 hexane, making a metallocene catalyst precursor on the
 surface of the support. Polymers were prepared using the
 preformed ZN catalyst and with the modified ZN catalyst
 prepared in accordance with this invention and the
 results are shown in samples 12 and 12a in Table D,
 respectively. The activity of the modified ZN catalyst
 is double the activity of the preformed, unmodified ZN

dichloride (20 mmol) as THF solutions were added. The slurry was mixed 1 hour at RT and dried in vacuo at 50°C.

General Polymerization Protocol
for Examples 15 through 25

5 A 2 litre Zipperclave® is purged with purified argon at 100°C for one hour. Heptane (500 mL) containing TEAL (500 mmol) and desired comonomer is added. The reactor
10 is saturated with the desired partial pressure of H₂ (60 psig unless otherwise noted) followed by ethylene up to 180 psig. After temperature equilibration is reached, the catalyst as a slurry in heptane (c. 20 mL) with TEAL (500 mmol) cocatalyst (or activator) is blown in under
15 argon pressure. Ethylene uptake and temperature are monitored. The polymerization is quenched by rapid release of the ethylene pressure followed by argon purging. The polymer is washed with MeOH, stabilized and dried for more than 16 hours in vacuo. In no case, when
20 products of the present invention were utilized, was any fouling of the reactor noted.

Examples 15-18 and 20-25 use a catalyst system incorporated the in-situ prepared Ex. 13 and TEAL as its activator. Examples 19 is physical mixture catalyst of
25 Ex. 14 activated with TEAL.

Varying Hydrogen Partial Pressure Using Ex. 13 Catalyst

Ex	Al (mmol)	Cat (g)	Ti (mmol/g)	Ti (mmol)	Al/ Ti	P (H ₂)	P (C ₂ =)	Y (g)	A
21	2	0.017	1.15	0.020	102	0	180	120	7
22	2	0.014	1.15	0.016	124	10	170	130	9
23	2	0.014	1.15	0.016	124	30	150	90	6
24	2	0.014	1.15	0.016	124	60	120	96	7
25	2	0.015	1.15	0.017	116	90	90	18	1.2

A=activity in kg PE/g cat-h

5 Figure 1 depicts a chromatogram of a polyethylene produced by a commercial Ziegler-Natta catalyst (Ex. 12).

10 Figure 2 depicts the resulting chromatogram of PE produced with the present invention: the catalyst used in Fig. 1 was treated with Cp₂Mg prior to polymerization of ethylene (Ex. 12a).

 Figure 3 depicts the chromatogram of polyethylene produced with the present invention in Example 22.

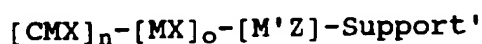
15 Figure 4 depicts the chromatogram of polyethylene produced with the present invention in Example 15.

COMPOSITIONAL ANALYSIS

20 In order to prove the difference in character of these two materials, each material was washed in separate Soxhlet extractors and extracted with toluene for a

I CLAIM:

1. A supported polyolefin catalytic precursor comprising comprising:



5 wherein,

Support' is selected from the group comprising porous inorganic, inorganic oxide or organic material;

C is defined as one five-member carbon ring, heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as multi-cyclic moieties capable of coordinating to the transition or rare earth metals, M;

10 M is selected from the group comprising Groups 3 through 10, lanthanides, actinides metals of the Periodic Table and mixtures thereof;

15 M' is selected from the group comprising Group 1, 2, 3 and 13 metals of the Periodic Table, wherein M' always contains an amount of Mg, Al, Zn and mixtures thereof such that the molar ratio of these elements in M' to M is at least 1:1;

20 X and Z may be the same or different are selected from the group comprising halogen group elements, halosubstituted and non-substituted alkoxys, alkyls, aryls, alkenyls, amides and mixtures of any two or more of the foregoing X's and Z's; and

25 wherein the composition has the following characteristics CMX is approximately 0.1% to 50%;

- 49 -

containing hydride, halogen radicals, and C1-20 hydrocarbyl radicals;

M is selected from the group comprising titanium, zirconium, hafnium, chromium, vanadium, samarium, neodymium and mixtures thereof; and

M' is selected from the group comprising preferably, Mg, Al, Zn, In, silicon, germanium, tin and mixtures thereof, wherein M' always contains an amount of Mg, Al, Zn and mixtures thereof such that the molar ratio of these elements in M' to M is 2:1 or greater;

X and Z are selected from the group comprising C1-C20 alkoxys, C1-C20 alkyls, C6-C20 aryls, C1-C20 alkenyls, amides of the formula NR^aR^b , wherein the R^a and R^b can be the same or different and independently selected from halosubstituted and non-substituted alkyls, alkenyls, aryls, or silanes, and mixtures of two or more of the foregoing X's or Z's; and

wherein the composition has the following characteristics CMX 0.1 - 10%; MX is 0.0-20%; and MZ is 5.0-50%.

- 51 -

4. The composition according to claim 3, wherein
Support' is selected from the group comprising
silica-alumina, silica-titania, silica-titania-alumina,
zeolite, ferrite, glass fibers, magnesia, titania,
zirconia, aluminum phosphate gel, silanized silica and
mixtures thereof;

C is dicyclopentadienyl;

M' is Mg;

M is Ti; and

X and Z are selected from the group comprising
chloride, bromide, and mixtures thereof, wherein n is
never 0.

5. A method for preparing a supported polyolefin
catalytic precursor, said method comprising the steps of
reacting reagents (i) and (ii) wherein

(i) is an organometallic compound of the formula
CM', and (ii) is represented by the formula MZ, wherein

C is defined as one five-member carbon ring,
heterosubstituted five-member carbon ring, or a bridged
(ansa) ligand defined as multi-cyclic moieties capable of
coordinating to the transition or rare earth metals, M;

M is selected from the group comprising Groups 3
through 10, lanthanides, actinides metals of the Periodic
Table and mixtures thereof;

- 53 -

M is selected from the group comprising titanium, zirconium, hafnium, chromium, vanadium, samarium, neodymium and mixtures thereof; and

5 M' is selected from the group comprising preferably, Mg, Al, Zn, In, silicon, germanium, tin and mixtures thereof, wherein M' always contains an amount of Mg, Al, Zn and mixtures thereof such that the molar ratio of these elements in M' to M is 2:1 or greater;

10 X and Z are selected from the group comprising C1-C20 alkoxys, C1-C20 alkyls, C6-C20 aryls, C1-C20 alkenyls, amides of the formula NR^aR^b , wherein the R^a and R^b can be the same or different and independently selected from halosubstituted and non-substituted alkyls, alkenyls, aryls, or silanes, and mixtures of two or more
15 of the foregoing X's or Z's; and

wherein the reagents are selected to result in a reaction composition having the following characteristics
CMX 0.1 - 10%; MX is 0.0-20%; and MZ is 5.0-50%.

9. The method according to Claims 5-8, wherein the reactants further including a Support selected from the from the group comprising $MgCl_2$, $MgCl(OEt)$, $Mg(OEt)_2$, organic magnesium compounds represent by $MgR'_xX'_y$ wherein, R' is is an alkyl group havng 1 to 20 carbon atoms, an alkoxy group having having 1 to 20 carbon atoms or aryl group having 6 to 20 carbon atoms; x is a halogen atom or an alkyl group having 1 to 20 carbon atoms; x is a number from 0 to 2; and y is a number from 0 to 2, talcs, clays, and metal oxides from Groups 2-14, actinide, lanthanide series metals, styrene-divinylbenzene copolymers, polyethylene, linear low density polyethylenes, polypropylene, polyvinylchloride, polyvinylalcohol, poly-4-methyl-1-pentene, substituted polystyrenes and polyarylates, starches and carbon and mixtures thereof;

CM' may contain X defined the same as Z and MZ may further contain C .

10. The method according to Claims 5-9 wherein the reagents further include A group comprising acid halides, metal halides, organic halides, carboxcyclic acids, esters, ethers, C1-C20 alkyaluminums, C1-C20 alkyl lithium, Grignard reagents, halogen gas, alumoxanes and mixtures thereof.

- 57 -

13. A method for preparing a supported polyolefin catalytic precursor, said method comprising the steps of reacting reagents (i), (ii), and (iii) wherein

(i) is an organometallic compound of the formula CH , and (ii) is represented by the formula $M'R$, and (iii) is MZ , wherein

C is defined as one five-member carbon ring, heterosubstituted five-member carbon ring, or a bridged (ansa) ligand defined as multi-cyclic moieties capable of coordinating to the transition or rare earth metals, M ;

M is selected from the group comprising Groups 3 through 10, lanthanides, actinides metals of the Periodic Table and mixtures thereof;

M' is selected from the group comprising Group 1, 2, 3 and 13 metals of the Periodic Table, wherein M' always contains an amount of Mg , Al , Zn and mixtures thereof such that the molar ratio of these elements in M' to M is at least 1:1;

H is hydrogen;

R is

X and Z may be the same or different are selected from the group comprising halogen group elements, halosubstituted and non-substituted alkoxys, alkyls, aryls, alkenyls, amides and mixtures of any two or more of the foregoing X 's and Z 's; and

alkenyls, amides of the formula NR^aR^b , wherein the R^a and R^b can be the same or different and independently selected from halosubstituted and non-substituted alkyls, alkenyls, aryls, or silanes, and mixtures of two or more of the foregoing X's or Z's; and

wherein the reagents are selected to result in a reaction composition having the following characteristics
CMX 0.1 - 10%; MX is 0.0-20%; and MZ is 5.0-50%.

- 61 -

17. The method according to Claims 13-16, wherein the reactants further including a Support selected from the from the group comprising $MgCl_2$, $MgCl(OEt)$, $Mg(OEt)_2$, organic magnesium compounds represent by $MgR'_xX'_y$ wherein, R' is is an alkyl group havng 1 to 20 carbon atoms, an alkoxy group having having 1 to 20 carbon atoms or aryl group having 6 to 20 carbon atoms; x is a halogen atom or an alkyl group having 1 to 20 carbon atoms; x is a number from 0 to 2; and y is a number from 0 to 2, talcs, clays, and metal oxides from Groups 2-14, actinide, lanthanide series metals, styrene-divinylbenzene copolymers, polyethylene, linear low density polyethylenes, polypropylene, polyvinylchloride, polyvinylalcohol, poly-4-methyl-1-pentene, substituted polystyrenes and polyarylates, starches and carbon and mixtures thereof;

CM' may contain X defined the same as Z and MZ may further contain C .

18. The method according to Claims 13-17 wherein the reagents further include A group comprising acid halides, metal halides, organic halides, carboxcyclic acids, esters, ethers, C1-C20 alkylaluminums, C1-C20 alkyl lithium, Grignard reagents, halogen gases, alumoxanes and mixtures thereof.

reaction zone, thereby polymerizing said olefinic compounds.

5 23. The process according to claim 22, wherein the reaction zone occurs in a slurry, solvent or gas phase polymerization reactor.

10 24. A polymer formed by polymerizing olefinic material in the presence of one or more catalysts as defined in claims 1-4 and a catalyst activator.

15 25. A polymer formed by polymerizing olefinic material in the presence of one or more catalysts prepared in accordance with claims 5 through 20 and a catalyst activator.

2 / 4

FIG. 2

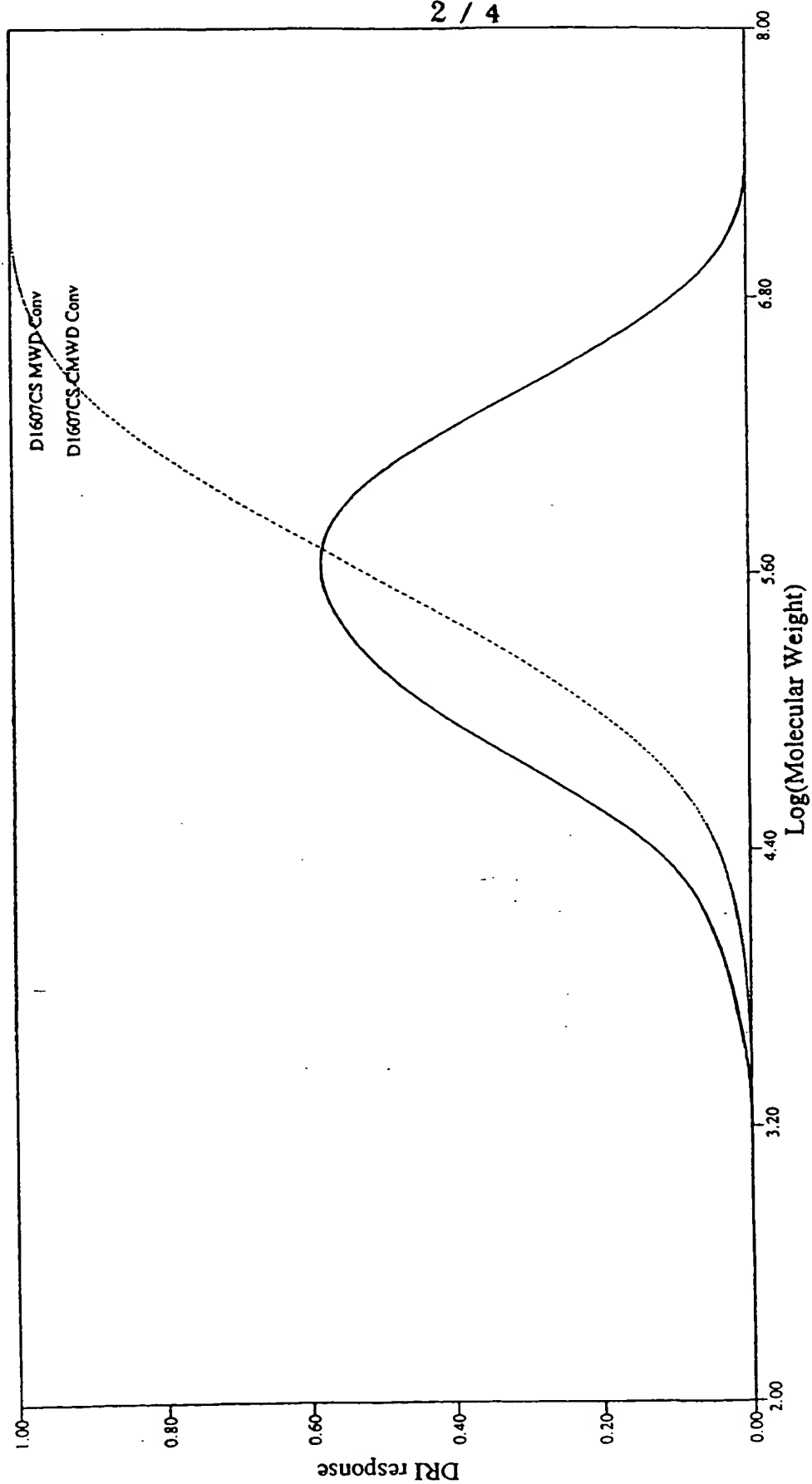
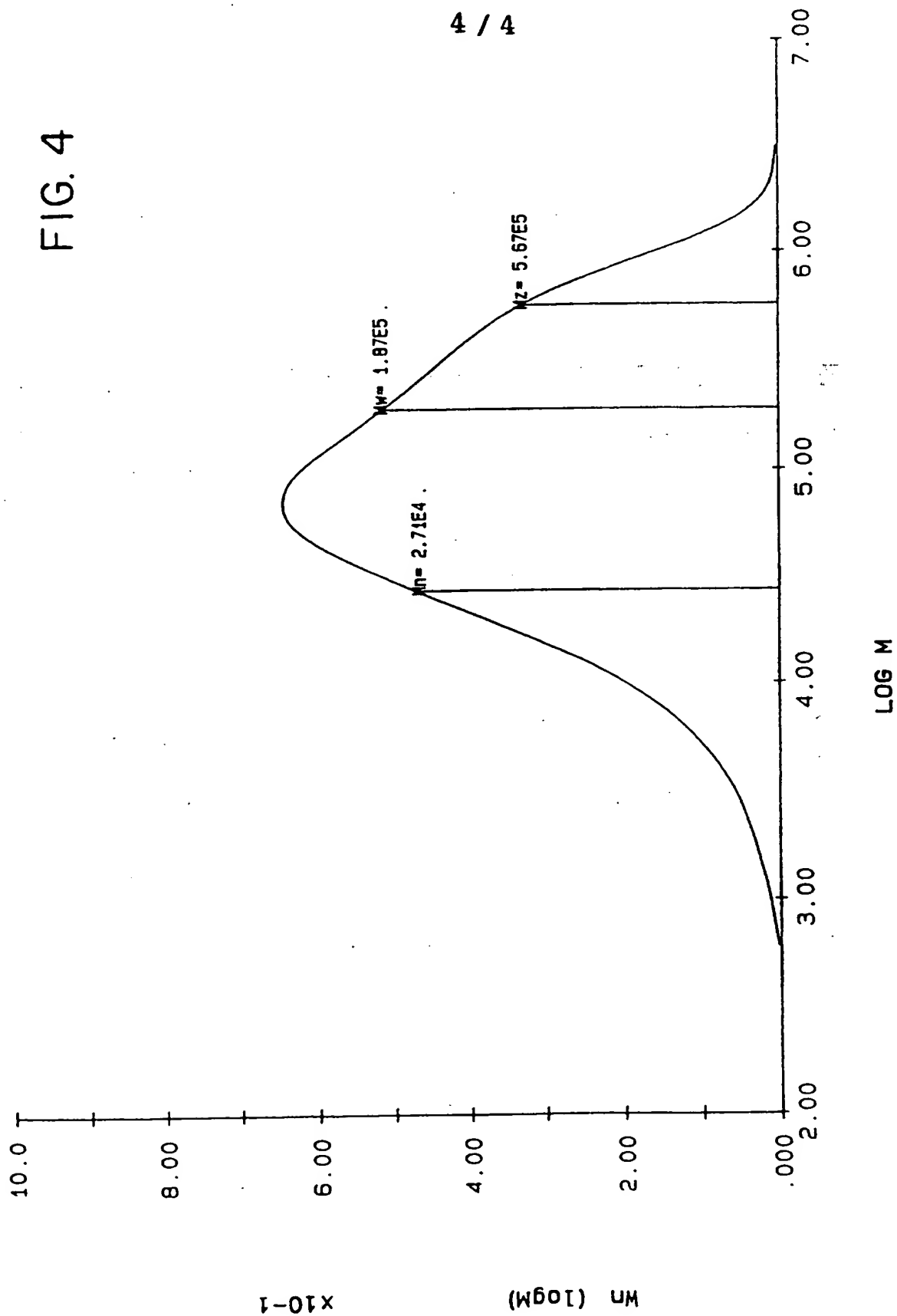


FIG. 4



INTERNATIONAL SEARCH REPORT

Inter. nal Application No
PCT/US 95/13148

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 436 328 (MITSUI TOATSU CHEMICALS) 10 July 1991 see example 1 see claims 1-11 ---	1,22-25
X	EP,A,0 412 750 (MITSUBISHI PETROCHEM KK) 13 February 1991 see claims 1-5,8-11 see example 9; table 2 ---	1,2, 22-25
X	EP,A,0 520 816 (NIPPON OIL CO LTD) 30 December 1992 see examples A05,6,9,21; table 1 ---	13-15, 21-25
X	EP,A,0 587 440 (NIPPON OIL CO LTD) 16 March 1994 see examples 32,43 ---	13,17, 18,21-25
A	EP,A,0 585 512 (FINA RESEARCH) 9 March 1994 see claims 1,9 see examples 1,3 -----	1-13, 20-25